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(71) Applicants:  
• UNILEVER PLC  
London EC4P 4BQ (GB)  
Designated Contracting States:  
GB IE CY  
• UNILEVER N.V.  
3013 AL Rotterdam (NL)  
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AT

(72) Inventors:  
• Delroisse, Michel Gilbert Jose  
Bebington, Wirral Merseyside CH63 3JW (GB)  
• Hage, Ronald  
Unilever Research Vlaardingen  
3133 AT Vlaardingen (NL)  
• Kalmeljer, Robertus Everardus  
3133 AT Vlaardingen (NL)  
• Lamers, Christiaan  
Unilever Research Vlaardingen  
3133 AT Vlaardingen (NL)

• Russell, Stephen William,  
Unilever Vlaardingen  
3133 AT Vlaardingen (NL)  
• Whittaker, Jane  
Bebington, Wirral Merseyside CH63 3JW (GB)  
• Feringa, Bernard Lucas  
University of Groningen  
Nijenborgh 4 9747 AG Groningen (NL)  
• Hermant, Roelant Mathijs  
Unilever Res. Vlaardingen  
3133 AT Vlaardingen (NL)  
• Koek, Jean Hypolites  
Unilever Res. Vlaardingen  
3133 AT Vlaardingen (NL)  
• Rispens, Minze Theunis  
University of Groningen  
Nijenborgh 4 9747 AG Groningen (NL)  
• van Vliet, Ronaldus Theodorus Leonardus  
3133 AT Vlaardingen (NL)

(74) Representative:  
Elliott, Peter William et al  
Unilever plc  
Patent Division  
Colworth House  
Sharnbrook  
Bedford MK44 1LQ (GB)

(54) Bleach and oxidation catalyst

(57) A bleach and oxidation catalyst is provided comprising a catalytically active iron, manganese or copper complex including a specified pentadentate nitrogen-containing ligand. The metal complex can activate hydrogen peroxide or peroxyacids and provides favourable stain removal properties. In addition, a considerably improved stability of these metal complex compounds in alkaline aqueous environment has been obtained, in particular at the peroxy compound concentrations generally present in the fabric washing liquor.

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**Description**Field of the Invention

5 [0001] This invention relates to bleach and oxidation catalysts, to compositions containing such catalysts, especially bleaching and detergent bleaching compositions, and to methods of bleaching and cleaning substrates, especially fabric substrates, using such catalysts. In particular, the present invention is concerned with catalytic complexes comprising a pentadentate ligand coordinated to an iron, manganese or copper ion, for use with peroxygen bleaching agents.

Background of the Invention.

[0002] Peroxygen bleaching agents have been known for many years and are used in a variety of industrial and domestic bleaching and cleaning processes. The activity of such agents is, however, extremely temperature-dependent, and drops off sharply at temperatures below 60°C. Especially for cleaning fabrics, high temperature operation is both economically undesirable and practically disadvantageous.

[0003] One approach to solving this problem has been through the additional use of so-called bleach activators, also known as bleach precursors. These activators typically are carboxylic acid esters that react with hydrogen peroxide anions in aqueous liquor to generate the corresponding peroxyacid which, in turn, oxidises the substrate. However, these activators are not catalytic. Once the activator has been perhydrolysed, it can no longer be recycled and, therefore, it is usually necessary to use relatively high levels of activator. Since bleach activators are relatively expensive, the cost of using activators at such levels may be prohibitive.

[0004] Another approach has been to use transition metal complexes as catalysts to activate the peroxy bleaching agent. For example, US-A-4,728,455 discloses the use of manganese(III)-gluconate as a peroxide bleach catalyst with high hydrolytic and oxidative stability. In EP-A-0,458,379, for example, triazacyclononane-based manganese complexes are disclosed that display a high catalytic oxidation activity at low temperatures, which is particularly suitable for bleaching purposes.

[0005] In WO-A-9534628, it has been shown that the use of iron complexes containing certain pentadentate nitrogen-containing ligands, in particular N,N-bis(pyridin-2-ylmethyl)-bis(pyridin-2-yl)methylamine ("N<sub>4</sub>Py"), as bleaching and oxidation catalysts, resulted in favourable bleaching and oxidation activity. However, the synthesis of this ligand is relatively costly.

[0006] WO-A-9718035 discloses iron and manganese complexes containing ligands such as N,N'-bis(pyridin-2-ylmethyl)ethylene-1,2-diamine ("Bispicen"), N-methyl-N,N',N'-tris(pyridin-2-ylmethyl)ethylene-1,2-diamine ("Trispic-Meen"), and N,N,N',N'-tetrakis(pyridin-2-ylmethyl)ethylene-1,2-diamine ("TPEN"), as peroxide oxidation catalysts for organic substrates.

[0007] WO-A-9748787 relates to iron complexes having polydentate ligands containing at least six nitrogen or oxygen hetero atoms, the metal ion being coordinated by at least five hetero atoms, for example 1,1,4,8,11,11-hexa(pyridin-2-ylmethyl)-1,4,8,11-tetra-aza-undecane ("Hptu"), as catalysts for peroxide, peroxyacid and molecular oxygen bleaching and oxidation.

[0008] Whilst known transition metal complexes have to an extent been used successfully as catalysts in bleaching or oxidation processes, there remains a need for other bleaching and oxidation catalysts, preferably that are more effective in terms of activity or cost.

[0009] We have now surprisingly found that a significant or improved catalytic activity can be achieved by an iron, manganese or copper complex having a pentadentate ligand comprising substituted heteroaryl groups. Furthermore, we have found that catalysts exhibiting such activity can be produced by easily accessible syntheses.

Summary of the Invention

[0010] Accordingly, in one aspect, the present invention provides a bleach and oxidation catalyst comprising a complex of the general formula (A):



in which

M represents iron in the II, III, IV or V oxidation state, manganese in the II, III, IV, VI or VII oxidation state, or copper in the I, II or III oxidation state;

X represents a coordinating species;

n represents zero or an integer in the range from 0 to 3;

z represents the charge of the complex and is an integer which can be positive, zero or negative;

Y represents a counter ion, the type of which is dependent on the charge of the complex;

$q = z/[\text{charge } Y]$ ;

5 L represents a pentadentate ligand of general formula (B):



wherein

10 each  $R^1$  independently represents  $-R^3-V$ , in which  $R^3$  represents optionally substituted alkylene, alkenylene, oxyalkylene, aminoalkylene or alkylene ether, and V represents a substituted heteroaryl group selected from pyridinyl, pyrazinyl, pyrazolyl, imidazolyl, benzimidazolyl, pyrimidinyl, triazolyl and thiazolyl;

W represents an optionally substituted alkylene bridging group selected from  $-CH_2CH_2-$ ,  $-CH_2CH_2CH_2-$ ,  $-CH_2CH_2CH_2CH_2-$ , and  $-CH_2-C_6H_4-CH_2-$ ;

15  $R^2$  represents a group selected from alkyl, aryl and arylalkyl, optionally substituted with a substituent selected from hydroxy, alkoxy, carboxylate, carboxamide, carboxylic ester, sulphonate, amine, alkylamine and  $N^+(R^4)_3$ , wherein  $R^4$  is selected from hydrogen, alkanyl, alkenyl, arylalkanyl, arylalkenyl, oxyalkanyl, oxyalkenyl, aminoalkanyl, aminoalkenyl, alkanyl ether and alkenyl ether.

20 **[0011]** In another aspect, the present invention provides a bleaching composition comprising a peroxy bleaching compound and a catalyst as defined above. The peroxy bleaching compound is preferably selected from hydrogen peroxide, hydrogen peroxide-liberating or -generating compounds, peroxyacids and their salts, and mixtures thereof. Preferably, the bleaching composition further comprises peroxyacid bleach precursors.

**[0012]** In yet another aspect, the present invention provides a detergent bleach composition comprising a peroxy bleaching compound and a catalyst as defined above, a surface-active material and a detergency builder.

25 **[0013]** Advantageously, complexes in accordance with the invention have been found to provide favourable stain removal in the presence of hydrogen peroxide or peroxyacids. Also, an improved bleaching activity has been noted, particularly in alkaline aqueous solutions containing peroxy compounds at concentrations generally present in the wash liquor during the fabric washing cycle. The complexes may also provide improved oxidation of organic substrates such as olefins, alcohols and unactivated hydrocarbons.

#### Detailed Description of the Invention

35 **[0014]** Generally, the metal-complex catalyst of the invention may be used in a bleaching system comprising a peroxy compound, optionally together with a precursor therefor, and is suitable for use in the washing and bleaching of substrates including laundry, dishwashing and hard surface cleaning. Alternatively, the metal-complex catalyst of the invention may be used for bleaching in the textile, paper and woodpulp industries, as well as in waste water treatment.

**[0015]** As already stated, an advantage of the catalysts according to the present invention is that they exhibit a remarkably high oxidation activity in alkaline aqueous media in the presence of peroxy compounds.

40 **[0016]** A second advantage of the catalysts of the invention is that they can show good bleaching activity at a broader pH range (generally pH 6-11) than those observed for the previously disclosed iron complexes. Their performance was especially improved at a pH of around 10. This advantage may be particularly beneficial in view of the current detergent formulations that employ rather alkaline conditions, as well as the tendency to shift the pH during fabric washing from alkaline (typically, a pH of 10) to more neutral values. Furthermore, this advantage can be beneficial when using the present catalysts in machine dishwash formulations.

45 **[0017]** Another advantage is that the catalysts of the invention have a relatively low molecular weight and, consequently, are very weight-effective.

**[0018]** The active metal-complex catalysts of the present invention may be dosed as well-defined complexes. Alternatively, the catalysts may be formed *in situ* from suitable precursors for the catalyst, for example in a solution or dispersion containing the precursor materials. In one such example, the active catalyst may be formed *in situ* in a mixture comprising a salt of the metal M and the ligand L, or a ligand L-generating species, in a suitable solvent. Thus, for example, if M is iron, an iron salt such as  $Fe(NO_3)_3$  can be mixed in solution with the ligand L, or a ligand L-generating species, to form the active metal complex. In another such example, the ligand L, or a ligand L-generating species, can be mixed with metal M ions present in the bleach or oxidation substrate or wash liquor to form the active catalyst *in situ*. 50 Suitable ligand L-generating species include metal-free compounds or metal coordination complexes that comprise the ligand L and can be substituted by metal M ions to form the active metal complex according to the formula (A).

55 **[0019]** Therefore, it will be appreciated that the catalyst in accordance with the present invention can be formed by any appropriate means, including *in situ* formation whereby precursors of the catalyst are transformed into the active

metal complex of general formula (A) under conditions of storage or use. Preferably, the catalyst is formed as a well-defined complex or in a solvent mixture comprising a salt of the metal M and the ligand L or ligand L-generating species.

[0020] The ligand L, having the general formula  $R^1R^1N-W-NR^1R^2$  as defined above, is a pentadentate ligand. By 'pentadentate' herein is meant that five hetero atoms can coordinate to the metal M ion in the metal-complex, of which two hetero atoms are linked by the bridging group W and one coordinating hetero atom is contained in each of the three  $R^1$  groups. Preferably, the coordinating hetero atoms are nitrogen atoms.

[0021] The ligand L comprises at least one substituted heteroaryl group in each of the three  $R^1$  groups. Preferably, the substituted heteroaryl group is a substituted pyridin-2-yl group, more preferably a methyl- or ethyl-substituted pyridin-2-yl group linked to an N atom in the above formula via a methylene group. More preferably, the substituted heteroaryl group is a 3-methyl-pyridin-2-yl group linked to an N atom via methylene. The group  $R^2$  is a substituted or unsubstituted alkyl, aryl or arylalkyl group, provided that  $R^2$  is different from each of the groups  $R^1$  in the formula above. Suitable substituents are selected from hydroxy, alkoxy, carboxylate, carboxamide, carboxylic ester, sulphonate, amine, alkylamine and  $N^+(R^4)_3$ , wherein  $R^4$  is selected from hydrogen, alkanyl, alkenyl, arylalkanyl, arylalkenyl, oxyalkanyl, oxyalkenyl, aminoalkanyl, aminoalkenyl, alkanyl ether and alkenyl ether. Preferably,  $R^2$  is methyl, ethyl, benzyl, 2-hydroxyethyl or 2-methoxyethyl. More preferably,  $R^2$  is methyl or ethyl.

[0022] The bridging group W may be a substituted or unsubstituted alkylene group selected from  $-CH_2CH_2-$ ,  $-CH_2CH_2CH_2-$ ,  $-CH_2CH_2CH_2CH_2-$ , and  $-CH_2-C_6H_4-CH_2-$  (wherein  $-C_6H_4-$  can be *ortho*-, *para*-, or *meta*- $C_6H_4$ ). Preferably, the bridging group is an ethylene or 1,4-butylene group, more preferably an ethylene group.

[0023] Examples of preferred ligands in their simplest forms are:

N-methyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;  
 N-ethyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;  
 N-benzyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;  
 N-(2-hydroxyethyl)-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;  
 N-(2-methoxyethyl)-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;  
 N-methyl-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;  
 N-ethyl-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;  
 N-benzyl-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;  
 N-(2-hydroxyethyl)-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;  
 N-(2-methoxyethyl)-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;  
 N-methyl-N,N',N'-tris(3-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;  
 N-ethyl-N,N',N'-tris(3-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;  
 N-benzyl-N,N',N'-tris(3-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;  
 N-(2-hydroxyethyl)-N,N',N'-tris(3-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;  
 N-(2-methoxyethyl)-N,N',N'-tris(3-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;  
 N-methyl-N,N',N'-tris(5-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;  
 N-ethyl-N,N',N'-tris(5-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;  
 N-benzyl-N,N',N'-tris(5-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine; and  
 N-(2-methoxyethyl)-N,N',N'-tris(5-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine.

[0024] More preferred ligands are:

N-methyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;  
 N-ethyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;  
 N-benzyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;  
 N-(2-hydroxyethyl)-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine; and  
 N-(2-methoxyethyl)-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine.

[0025] The most preferred ligands are:

N-methyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine; and  
 N-ethyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine.

[0026] The metal-complex catalysts according to the invention may include suitable counter ions to balance the charge  $z$  on the complex formed by the ligand L, metal M and coordinating species X. Thus, if the charge  $z$  is positive, Y may be an anion such as  $R^6COO^-$ ,  $BPh_4^-$ ,  $ClO_4^-$ ,  $BF_4^-$ ,  $PF_6^-$ ,  $R^6SO_3^-$ ,  $R^6SO_4^-$ ,  $SO_4^{2-}$ ,  $NO_3^-$ ,  $F^-$ ,  $Cl^-$ ,  $Br^-$ , or  $I^-$ , with  $R^6$  being hydrogen, optionally substituted alkyl or optionally substituted aryl. If  $z$  is negative, Y may be a common cation

such as an alkali metal, alkaline earth metal or (alkyl)ammonium cation.

[0027] Suitable counter ions Y include those which give rise to the formation of storage-stable solids. Preferred counter ions for the preferred metal complexes are selected from  $R^6\text{COO}^-$ ,  $\text{ClO}_4^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $R^6\text{SO}_3^-$  (in particular  $\text{CF}_3\text{SO}_3^-$ ),  $R^6\text{SO}_4^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  with  $R^6$  being hydrogen, optionally substituted phenyl, naphthyl or  $\text{C}_1$ - $\text{C}_4$  alkyl.

[0028] Suitable coordinating species X may be selected from  $R^5\text{OH}$ ,  $\text{NR}^5_3$ ,  $R^5\text{CN}$ ,  $R^5\text{OO}^-$ ,  $R^5\text{S}^-$ ,  $R^5\text{O}^-$ ,  $R^5\text{COO}^-$ ,  $\text{OCN}^-$ ,  $\text{SCN}^-$ ,  $\text{N}_3^-$ ,  $\text{CN}^-$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{O}^{2-}$ ,  $\text{O}_2^{2-}$ ,  $\text{O}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{PO}_4^{3-}$  and aromatic N donors selected from pyridines, pyrazines, pyrazoles, imidazoles, benzimidazoles, pyrimidines, triazoles and thiazoles, with  $R^5$  being selected from hydrogen, optionally substituted alkyl and optionally substituted aryl. X may also be the species  $\text{LMO}^-$  or  $\text{LMOO}^-$ , wherein M is a transition metal and L is a ligand as defined above. Preferred coordinating species X are  $\text{CH}_3\text{CN}$ ,  $\text{H}_2\text{O}$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{OOH}^-$ ,  $\text{O}_2^{2-}$ ,  $\text{O}_2^-$ ,  $\text{LMO}^-$ ,  $\text{LMOO}^-$ ,  $R^5\text{COO}^-$  and  $R^5\text{O}^-$  wherein  $R^5$  represents hydrogen or optionally substituted phenyl, naphthyl, or  $\text{C}_1$ - $\text{C}_4$  alkyl.

[0029] The effective level of the metal-complex catalyst, expressed in terms of parts per million (ppm) of metal M in an aqueous bleaching solution, will normally range from 0.001 ppm to 100 ppm, preferably from 0.01 ppm to 20 ppm, most preferably from 0.1 ppm to 10 ppm. Higher levels may be desired and applied in industrial bleaching processes, such as textile and paper pulp bleaching. The lower range levels are preferably used in domestic laundry operations.

[0030] The metal M may be selected from iron (Fe), manganese (Mn) and copper (Cu). Preferably, the metal is Fe or Mn, and more preferably Fe.

#### 20 The peroxy bleaching compound

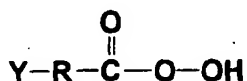
[0031] The peroxy bleaching compound may be any compound which is capable of yielding hydrogen peroxide in aqueous solution, including hydrogen peroxide and hydrogen peroxide adducts. Hydrogen peroxide sources are well known in the art. They include the alkali metal peroxides, organic peroxides such as urea peroxide, and inorganic per-salts, such as the alkali metal perborates, percarbonates, perphosphates, persulfates and persulfates. Mixtures of two or more such compounds may also be suitable.

[0032] Particularly preferred are sodium perborate tetrahydrate and, especially, sodium perborate monohydrate. Sodium perborate monohydrate is preferred because of its high active oxygen content. Sodium percarbonate may also be preferred for environmental reasons. The amount thereof in the composition of the invention usually will be within the range of about 2 to 35 % by weight, preferably from 10 to 25 % by weight.

[0033] Another suitable hydrogen peroxide generating system is a combination of a  $\text{C}_1$ - $\text{C}_4$  alkanol oxidase and a  $\text{C}_1$ - $\text{C}_4$  alkanol, especially a combination of methanol oxidase (MOX) and ethanol. Such combinations are disclosed in WO-A-9507972, which is incorporated herein by reference. A further suitable hydrogen peroxide generating system uses a combination of glucose oxidase and glucose.

[0034] Alkylhydroxy peroxides are another class of suitable peroxy bleaching compounds. Examples of these materials include cumene hydroperoxide and t-butyl hydroperoxide.

[0035] Organic peroxyacids are also suitable as peroxy bleaching compounds. Such materials normally have the general formula:



wherein R is an alkylene or alkyl- or alkylidene-substituted alkylene group containing from 1 to about 20 carbon atoms, optionally having an internal amide linkage; or a phenylene or substituted phenylene group; and Y is hydrogen, halogen, alkyl, aryl, an imido-aromatic or non-aromatic group, a  $-\text{COOH}$  or  $-\text{COOOH}$  group or a quaternary ammonium group.

[0036] Typical monoperoxyacids useful herein include, for example:

- 50 (i) peroxybenzoic acid and ring-substituted peroxybenzoic acids, e.g. peroxy- $\alpha$ -naphthoic acid;
- (ii) aliphatic, substituted aliphatic and arylalkyl monoperoxyacids, e.g. peroxy lauric acid, peroxy stearic acid and N,N-phthaloylaminoperoxy caproic acid (PAP); and
- (iii) 6-octylamino-6-oxo-peroxyhexanoic acid.

55 [0037] Typical diperoxyacids useful herein include, for example:

- (iv) 1,12-diperoxydodecanedioic acid (DPDA);
- (v) 1,9-diperoxyazelaic acid;

- (vi) diperoxybrassylic acid; diperoxysebacic acid and diperoxyisophthalic acid;
- (vii) 2-decyldiperoxybutane-1,4-dioic acid; and
- (viii) 4,4'-sulphonylbisperoxybenzoic acid.

5 [0038] Also suitable are inorganic peroxyacid compounds such as, for example, potassium monopersulphate (MPS). If organic or inorganic peroxyacids are used as the peroxygen compound, the amount thereof will normally be within the range of about 2 to 10 % by weight, preferably from 4 to 8 % by weight.

[0039] Generally, the bleaching composition of the invention can be suitably formulated to contain from 2 to 35 %, preferably from 5 to 25 % by weight, of the peroxy bleaching compound.

10 [0040] All these peroxy compounds may be utilized either alone or in conjunction with a peroxyacid bleach precursor and/or an organic bleach catalyst not containing a transition metal.

[0041] Peroxyacid bleach precursors are known and amply described in literature, such as in the GB-A-0,836,988; GB-A-0,864,798; GB-A-0,907,356; GB-A-1,003,310 and GB-A-1,519,351; DE-A-3,337,921; EP-A-0,185,522; EP-A-0,174,132; EP-A-0,120,591; and US-A-1,246,339; US-A-3,332,882; US-A-4,128,494; US-A-4,412,934 and US-A-4,675,393.

[0042] Another useful class of peroxyacid bleach precursors is that of the cationic *i.e.* quaternary ammonium substituted peroxyacid precursors as disclosed in US-A-4,751,015 and US-A-4,397,757, in EP-A-0,284,292 and EP-A-0,331,229. Examples of peroxyacid bleach precursors of this class are:

- 20 2-(N,N,N-trimethyl ammonium)ethyl sodium-4-sulphophenyl carbonate chloride - (SPCC);
- N-octyl-N,N-dimethyl-N<sub>10</sub>-carbophenoxy decyl ammonium chloride - (ODC);
- 3-(N,N,N-trimethyl ammonium) propyl sodium-4-sulphophenyl carboxylate; and
- N,N,N-trimethyl ammonium toluoyloxy benzene sulphonate.

25 [0043] A further special class of bleach precursors is formed by the cationic nitriles as disclosed in EP-A-0,303,520; EP-A-0,458,396 and EP-A-0,464,880.

[0044] Any one of these peroxyacid bleach precursors can be used in the present invention, though some may be more preferred than others. Of the above classes of bleach precursors, the preferred classes are the esters, including acyl phenol sulphonates and acyl alkyl phenol sulphonates; the acyl-amides; and the quaternary ammonium substituted peroxyacid precursors including the cationic nitriles.

30 [0045] Examples of the preferred peroxyacid bleach precursors or activators are sodium-4-benzoyloxy benzene sulphonate (SBOBS); N,N,N'-tetraacetyl ethylene diamine (TAED); sodium-1-methyl-2-benzoyloxy benzene-4-sulphonate; sodium-4-methyl-3-benzoyloxy benzoate; 2-(N,N,N-trimethyl ammonium)ethyl sodium-4-sulphophenyl carbonate chloride (SPCC); trimethyl ammonium toluoyloxy-benzene sulphonate; sodium nonanoyloxybenzene sulphonate (SNOBS); sodium 3,5,5-trimethyl hexanoyl-oxybenzene sulphonate (STHOBS); and the substituted cationic nitriles.

35 [0046] The precursors may be used in an amount of up to 12 %, preferably from 2 to 10 % by weight, of the composition.

#### The detergent bleach composition

40 [0047] The bleaching composition of the invention has particular application in detergent formulations. Accordingly, in another aspect, the invention provides a detergent bleach composition comprising a peroxy bleaching compound as defined above, the aforesaid metal-complex catalyst having the general formula (A), a surface-active material and a detergency builder.

45 [0048] The metal-complex catalyst will be present in the detergent bleach composition of the invention in amounts so as to provide the required level in the wash liquor. Generally, the metal-complex catalyst level in the detergent bleach composition corresponds to an iron, manganese or copper content of from 0.0005% to 0.5% by weight. When the dosage of detergent bleach composition is relatively low, *e.g.* about 1 to 2 g/l, the metal content in the formulation is suitably 0.0025 to 0.5%, preferably 0.005 to 0.25% by weight. At higher product dosages, as used for example by European consumers, the metal content in the formulation is suitably 0.0005 to 0.1%, preferably 0.001 to 0.05% by weight.

50 [0049] Detergent bleach compositions of the invention are effective over a wide pH-range of between 7 and 13, with optimal pH-range lying between 8 and 11.

#### The surface-active material

55 [0050] The detergent bleach composition according to the present invention generally contains a surface-active material in an amount of from 10 to 50% by weight. The surface-active material may be naturally derived, such as soap, or a synthetic material selected from anionic, nonionic, amphoteric, zwitterionic, cationic actives and mixtures thereof

Many suitable actives are commercially available and are fully described in the literature, for example in "Surface Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

[0051] Typical synthetic anionic surface-active compounds are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher aryl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and ammonium alkyl sulphates, especially those obtained by sulphating higher ( $C_8$ - $C_{18}$ ) alcohols produced, for example, from tallow or coconut oil; sodium and ammonium alkyl ( $C_9$ - $C_{20}$ ) benzene sulphonates, particularly sodium linear secondary alkyl ( $C_{10}$ - $C_{15}$ ) benzene sulphonates; sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil fatty acid monoglyceride sulphates and sulphonates; sodium and ammonium salts of sulphuric acid esters of higher ( $C_9$ - $C_{18}$ ) fatty alcohol alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralised with sodium hydroxide; sodium and ammonium salts of fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by reacting alpha-olefins ( $C_8$ - $C_{20}$ ) with sodium bisulphite and those derived by reacting paraffins with  $SO_2$  and  $Cl_2$  and then hydrolysing with a base to produce a random sulphonate; sodium and ammonium ( $C_7$ - $C_{12}$ ) dialkyl sulphosuccinates; and olefin sulphonates, which term is used to describe material made by reacting olefins, particularly ( $C_{10}$ - $C_{20}$ ) alpha-olefins, with  $SO_3$  and then neutralising and hydrolysing the reaction product. The preferred anionic detergent compounds are sodium ( $C_{10}$ - $C_{15}$ ) alkylbenzene sulphonates, and sodium ( $C_{16}$ - $C_{18}$ ) alkyl ether sulphates.

[0052] Examples of suitable nonionic surface-active compounds which may be used, preferably together with the anionic surface-active compounds, include, in particular, the reaction products of alkylene oxides, usually ethylene oxide, with alkyl ( $C_6$ - $C_{22}$ ) phenols, generally 5-25 EO, i.e. 5-25 units of ethylene oxides per molecule; and the condensation products of aliphatic ( $C_8$ - $C_{18}$ ) primary or secondary linear or branched alcohols with ethylene oxide, generally 2-30 EO. Other so-called nonionic surface-actives include alkyl polyglycosides, sugar esters, long-chain tertiary amine oxides, long-chain tertiary phosphine oxides and dialkyl sulphoxides.

[0053] Amphoteric or zwitterionic surface-active compounds can also be used in the compositions of the invention but this is not normally desired owing to their relatively high cost. If any amphoteric or zwitterionic detergent compounds are used, it is generally in small amounts in compositions based on the much more commonly used synthetic anionic and nonionic actives.

[0054] The detergent bleach composition of the invention will preferably comprise from 1 to 15 % wt of anionic surfactant and from 10 to 40 % by weight of nonionic surfactant. In a further preferred embodiment, the detergent active system is free from  $C_{16}$ - $C_{12}$  fatty acid soaps.

#### The detergency builder

[0055] The detergent bleach composition of the invention normally and preferably also contains a detergency builder in an amount of from about 5 to 80 % by weight, preferably from about 10 to 60 % by weight.

[0056] Builder materials may be selected from 1) calcium sequestrant materials, 2) precipitating materials, 3) calcium ion-exchange materials and 4) mixtures thereof.

[0057] Examples of calcium sequestrant builder materials include alkali metal polyphosphates, such as sodium tripolyphosphate; nitrilotriacetic acid and its water-soluble salts; the alkali metal salts of carboxymethyloxy succinic acid, ethylene diamine tetraacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, citric acid; and polyacetal carboxylates as disclosed in US-A-4,144,226 and US-A-4,146,495.

[0058] Examples of precipitating builder materials include sodium orthophosphate and sodium carbonate.

[0059] Examples of calcium ion-exchange builder materials include the various types of water-insoluble crystalline or amorphous aluminosilicates, of which zeolites are the best known representatives, e.g. zeolite A, zeolite B (also known as zeolite P), zeolite C, zeolite X, zeolite Y and also the zeolite P-type as described in EP-A-0,384,070.

[0060] In particular, the compositions of the invention may contain any one of the organic and inorganic builder materials, though, for environmental reasons, phosphate builders are preferably omitted or only used in very small amounts. Typical builders usable in the present invention are, for example, sodium carbonate, calcite/carbonate, the sodium salt of nitrilotriacetic acid, sodium citrate, carboxymethyloxy malonate, carboxymethyloxy succinate and water-insoluble crystalline or amorphous aluminosilicate builder materials, each of which can be used as the main builder, either alone or in admixture with minor amounts of other builders or polymers as co-builder.

[0061] It is preferred that the composition contains not more than 5% by weight of a carbonate builder, expressed as sodium carbonate, more preferably not more than 2.5 % by weight to substantially nil, if the composition pH lies in the lower alkaline region of up to 10.

Other ingredients

[0062] Apart from the components already mentioned, the detergent bleach composition of the invention can contain any of the conventional additives in amounts of which such materials are normally employed in fabric washing detergent compositions. Examples of these additives include buffers such as carbonates, lather boosters, such as alkanolamides, particularly the monoethanol amides derived from palmkernel fatty acids and coconut fatty acids; lather depressants, such as alkyl phosphates and silicones; anti-redeposition agents, such as sodium carboxymethyl cellulose and alkyl or substituted alkyl cellulose ethers; stabilizers, such as phosphonic acid derivatives (*i.e.* Dequest® types); fabric softening agents; inorganic salts and alkaline buffering agents, such as sodium sulphate and sodium silicate; and, usually in very small amounts, fluorescent agents; perfumes; enzymes, such as proteases, cellulases, lipases, amylases and oxidases; germicides and colourants.

[0063] When using a hydrogen peroxide source, such as sodium perborate or sodium percarbonate, as the bleaching compound, it is preferred that the composition contains not more than 5 % by weight of a carbonate buffer, expressed as sodium carbonate, more preferable not more than 2.5% by weight to substantially nil, if the composition pH lies in the lower alkaline region of up to 10.

[0064] Of the additives, transition metal sequestrants such as EDTA, and phosphonic acid derivatives such as EDTMP (ethylene diamine tetra(methylene phosphonate)) are of special importance, as not only do they improve the stability of the catalyst/H<sub>2</sub>O<sub>2</sub> system and sensitive ingredients, such as enzymes, fluorescent agents, perfumes and the like, but also improve the bleach performance, especially at the higher pH region of above 10, particularly at pH 10.5 and above.

[0065] The invention will now be further illustrated by way of the following non-limiting examples:

EXAMPLES25 Synthesis:

[0066] All reactions were performed under a nitrogen atmosphere, unless indicated otherwise. All reagents and solvents were obtained from Aldrich or Across and used as received, unless stated otherwise. Petroleum ether 40-60 was distilled using a rotavapor before using it as eluent. Flash column chromatography was performed using Merck silica gel 60 or aluminium oxide 90 (activity II-III according to Brockmann). <sup>1</sup>H NMR (300 MHz) and <sup>13</sup>C NMR (75 MHz) were recorded in CDCl<sub>3</sub>, unless stated otherwise. Multiplicities were addressed with the normal abbreviations using p for quintet.

Synthesis of starting materials for ligand synthesis:

35 [0067] **Synthesis of *N*-benzyl amino acetonitrile.** *N*-benzyl amine (5.35 g, 50 mmol) was dissolved in a water: methanol mixture (50 mL, 1:4). Hydrochloric acid (aq., 30 %) was added until the pH reached 7.0. Added was NaCN (2.45 g, 50 mmol). After cooling to 0 °C, formaline (aq. 35 %, 4.00 g, 50 mmol) was added. The reaction was followed by TLC (aluminium oxide; EtOAc : Et<sub>3</sub>N = 9:1) until benzylamine could be detected. Subsequently the methanol was 40 evaporated *in vacuo* and the remaining oil "dissolved" in water. The aqueous phase was extracted with methylene chloride (3 x 50 mL). The organic layers were collected and the solvent removed *in vacuo*. The residue was purified by Kugelrohr distillation (p = 20 mm Hg, T 120 °C) giving *N*-benzyl amino acetonitrile (4.39 g, 30 mmol, 60 %) as a colourless oil.

45 <sup>1</sup>H NMR: δ 7.37 - 7.30 (m, 5H), 3.94 (s, 2H), 3.57 (s, 2H), 1.67 (br s, 1H),  
<sup>13</sup>C NMR: δ 137.74, 128.58, 128.46, 128.37, 127.98, 127.62, 117.60, 52.24, 36.19.

[0068] **Synthesis of *N*-ethyl amino acetonitrile.** This synthesis was performed analogously to the synthesis reported for *N*-benzyl amino acetonitrile. However, detection was done by dipping the TLC plate in a solution of KMnO<sub>4</sub> and heating the plate until bright spots appeared. Starting from ethylamine (2.25 g, 50 mmol), pure *N*-ethyl amino acetonitrile (0.68 g, 8.1 mmol, 16 %) was obtained as a slightly yellow oil.

<sup>1</sup>H NMR: δ 3.60 (s, 2H), 2.78 (q, *J* = 7.1, 2H), 1.22 (br s, 1H), 1.14 (t, *J* = 7.2, 3H);  
<sup>13</sup>C NMR: δ 117.78, 43.08, 37.01, 14.53.

55 [0069] **Synthesis of *N*-ethyl ethylene-1,2-diamine.** The synthesis was performed according to Hageman; J.Org.Chem.; 14; 1949; 616, 634, starting from *N*-ethyl amino acetonitrile.

[0070] **Synthesis of *N*-benzyl ethylene-1,2-diamine.** Sodium hydroxide (890 mg; 22.4 mmol) was dissolved in



ethanol (96 %, 20 mL), the process taking the better part of 2 hours. Added was *N*-benzyl amino acetonitrile (4, 2.92 g, 20 mmol) and Raney Nickel (approx. 0.5 g). Hydrogen pressure was applied ( $p = 3.0$  atm.) until hydrogen uptake ceased. The mixture was filtered over Cellite, washing the residue with ethanol. The filter should not run dry since Raney Nickel is relatively pyrophoric. The Cellite containing the Raney Nickel was destroyed by putting the mixture in dilute acid, causing gas formation). The ethanol was evaporated in *in vacuo* and the residue dissolved in water. Upon addition of base (aq. NaOH, 5N) the product oiled out and was extracted with chloroform (3 x 20 mL). After evaporation of the solvent *in vacuo* the  $^1\text{H}$  NMR showed the presence of benzylamine. Separation was enforced by column chromatography (silica gel; MeOH : EtOAc : Et<sub>3</sub>N = 1:8:1) yielding the benzyl amine, followed by the solvent mixture MeOH : EtOAc : Et<sub>3</sub>N = 5:4:1. Detection was done by using aluminium oxide as a solid phase in TLC, yielding pure *N*-benzyl ethylene-1,2-diamine (2.04 g, 13.6 mmol, 69 %).

$^1\text{H}$  NMR:  $\delta$  7.33 -7.24 (m, 5H), 3.80 (s, 2H), 2.82 (t,  $J = 5.7$ , 2H), 2.69 (t,  $J = 5.7$ , 2H), 1.46 (br s, 3H);  
 $^{13}\text{C}$  NMR:  $\delta$  140.37, 128.22, 127.93, 126.73, 53.73, 51.88, 41.66.

**[0071] Synthesis of 2-acetoxymethyl-5-methyl pyridine.** 2,5-Lutidine (31.0 g, 290 mmol), acetic acid (180 mL) and hydrogen peroxide (30 mL, 30 %) were heated at 70-80 °C for 3 hours. Hydrogen peroxide (24 mL, 30 %) was added and the subsequent mixture heated for 16 hours at 60-70 °C. Most of the mixture of (probably) hydrogen peroxide, water, acetic acid, and peracetic acid was removed *in vacuo* (rotavap, water bath 50 °C until  $p = 20$  mbar). The resulting mixture containing the *N*-oxide was added dropwise to acetic anhydride heated under reflux. This reaction was highly exothermic, and was controlled by the dropping speed. After heating under reflux for an hour, methanol was added dropwise. This reaction was highly exothermic. The resulting mixture was heated under reflux for another 30 minutes. After evaporation of the methanol (rotavap, 50 °C until  $p = 20$  mbar), the resulting mixture was purified by Kugelrohr distillation ( $p = 20$  mm Hg,  $T = 150$  °C). The clear oil that was obtained still contained acetic acid. This was removed by extraction ( $\text{CH}_2\text{Cl}_2$ ,  $\text{NaHCO}_3$  (sat.)) yielding the pure acetate of 2-acetoxymethyl-5-methyl pyridine (34.35 g, 208 mmol, 72 %) as a slightly yellow oil.

$^1\text{H}$  NMR:  $\delta$  8.43 (s, 1H), 7.52 (dd,  $J = 7.8$ ,  $J = 1.7$ , 1H), 7.26 (d,  $J = 7.2$ , 1H), 5.18 (s, 2H), 2.34 (s, 3H), 2.15 (s, 3H);  
 $^{13}\text{C}$  NMR:  $\delta$  170.09, 152.32, 149.39, 136.74, 131.98, 121.14, 66.31, 20.39, 17.66.

**[0072] Synthesis of 2-acetoxymethyl-5-ethyl pyridine.** This synthesis was performed analogously to the synthesis reported for 2-acetoxymethyl-5-methyl pyridine. Starting from 5-ethyl-2-methyl pyridine (35.10 g, 290 mmol), pure 2-acetoxymethyl-5-ethyl pyridine (46.19 g, 258 mmol, 89%) was obtained as a slightly yellow oil.

$^1\text{H}$  NMR:  $\delta$  8.47 (s, 1H), 7.55 (d,  $J = 7.8$ , 1H), 7.29 (d,  $J = 8.1$ , 1H), 2.67 (q,  $J = 7.8$ , 2H), 2.14 (s, 3H), 1.26 (t,  $J = 7.77$ , 3H);  
 $^{13}\text{C}$  NMR:  $\delta$  170.56, 152.80, 149.11, 138.47, 135.89, 121.67, 66.72, 25.65, 20.78, 15.13.

**[0073] Synthesis of 2-acetoxymethyl-3-methyl pyridine.** This synthesis was performed analogously to the synthesis reported for 2-acetoxymethyl-5-methyl pyridine. The only difference was the reversal of the Kugelrohr distillation and the extraction. According to  $^1\text{H}$  NMR a mixture of the acetate and the corresponding alcohol was obtained. Starting from 2,3-picoline (31.0 g, 290 mmol), pure 2-acetoxymethyl-3-methyl pyridine (46.19 g, 258 mmol, 89%, calculated for pure acetate) was obtained as a slightly yellow oil.

$^1\text{H}$  NMR:  $\delta$  8.45 (d,  $J = 3.9$ , 1H), 7.50 (d,  $J = 8.4$ , 1H), 7.17 (dd,  $J = 7.8$ ,  $J = 4.8$ , 1H), 5.24 (s, 2H), 2.37 (s, 3H), 2.14 (s, 3H).

**[0074] Synthesis of 2-hydroxymethyl-5-methyl pyridine.** 2-Acetoxymethyl-5-methyl pyridine (30 g, 182 mmol) was dissolved in hydrochloric acid (100 mL, 4 N). The mixture was heated under reflux, until TLC (silica gel; triethylamine:ethyl acetate:petroleum ether 40-60 = 1:9:19) showed complete absence of the acetate (normally 1 hour). The mixture was cooled, brought to pH > 11, extracted with dichloromethane (3 x 50 mL) and the solvent removed *in vacuo*. Pure 2-hydroxymethyl-5-methyl pyridine (18.80 g, 152 mmol, 84 %) was obtained by Kugelrohr distillation ( $p = 20$  mm Hg,  $T = 130$  °C) as a slightly yellow oil.

$^1\text{H}$  NMR:  $\delta$  8.39 (s, 1H), 7.50 (dd,  $J = 7.8$ ,  $J = 1.8$ , 1H), 7.15 (d,  $J = 8.1$ , 1H), 4.73 (s, 2H), 3.83 (br s, 1H), 2.34 (s, 3H);  
 $^{13}\text{C}$  NMR:  $\delta$  156.67, 148.66, 137.32, 131.62, 120.24, 64.12, 17.98.

**[0075] Synthesis of 2-hydroxymethyl-5-ethyl pyridine.** This synthesis was performed analogously to the synthe-

sis reported for 2-hydroxymethyl-5-methyl pyridine. Starting from 2-acetoxymethyl-5-ethyl pyridine (40 g, 223 mmol), pure 2-hydroxymethyl-5-ethyl pyridine (26.02 g, 189 mmol, 85 %) was obtained as a slightly yellow oil.

<sup>1</sup>H NMR: δ 8.40 (d, *J* = 1.2, 1H), 7.52 (dd, *J* = 8.0, *J* = 2.0, 1H), 7.18 (d, *J* = 8.1, 1H), 4.74 (s, 2H), 3.93 (br s, 1H), 2.66 (q, *J* = 7.6, 2H), 1.26 (t, *J* = 7.5, 3H);  
<sup>13</sup>C NMR: δ 156.67, 148.00, 137.87, 136.13, 120.27, 64.07, 25.67, 15.28.

**[0076] Synthesis of 2-hydroxymethyl-3-methyl pyridine.** This synthesis was performed analogously to the synthesis reported for 2-hydroxymethyl-5-methyl pyridine. Starting from 2-acetoxymethyl-3-methyl pyridine (25g (recalculated for the mixture), 152 mmol), pure 2-hydroxymethyl-3-methyl pyridine (15.51 g, 126 mmol, 83 %) was obtained as a slightly yellow oil.

<sup>1</sup>H NMR: δ 8.40 (d, *J* = 4.5, 1H), 7.47 (d, *J* = 7.2, 1H), 7.15 (dd, *J* = 7.5, *J* = 5.1, 1H), 4.85 (br s, 1H), 4.69 (s, 1H), 2.22 (s, 3H);  
<sup>13</sup>C NMR: δ 156.06, 144.97, 137.38, 129.53, 121.91, 61.38, 16.30.

#### Synthesis of Ligands:

**[0077] Synthesis of *N*-methyl-*N,N,N*'-tris(pyridin-2-ylmethyl)ethylene-1,2-diamine (L1).** The ligand L1 (comparative) was prepared according to Bernal, Ivan; Jensen, Inge Margrethe; Jensen, Kenneth B.; McKenzie, Christine J.; Toftlund, Hans; Tuchagues, Jean-Pierre; J.Chem.Soc.Dalton Trans.; 22; 1995; 3667-3676.

**[0078] Synthesis of *N*-methyl-*N,N,N*'-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine (L2, Me-TRILEN).** 2-Hydroxymethyl-3-methyl pyridine (5.00 g, 40.7 mmol) was dissolved in dichloromethane (30 mL). Thionyl chloride (30 mL) was added dropwise under cooling (ice bath). The resulting mixture was stirred for 1 hour and the solvents removed *in vacuo* (rotavap, until *p* = 20 mm Hg, *T* = 50 °C). To the resultant mixture was added dichloromethane (25 mL). Subsequently NaOH (5 N, aq.) was added dropwise until the pH (aqua) ≥ 11. The reaction was quite vigorous in the beginning, since part of the thionyl chloride was still present. *N*-methyl ethylene-1,2-diamine (502 mg, 6.8 mmol) and additional NaOH (5 N, 10 mL) were added. The reaction mixture was stirred at room temperature for 45 hours. The mixture was poured into water (200 mL), and the pH checked (≥ 14, otherwise addition of NaOH (aq. 5N)). The reaction mixture was extracted with dichloromethane (3 or 4 x 50 mL, until no product could be detected by TLC). The combined organic phases were dried and the solvent removed *in vacuo*. Purification was enforced as described before, yielding *N*-methyl-*N,N,N*'-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine as a slightly yellow oil. Purification was enforced by column chromatography (aluminium oxide 90 (activity II-III according to Brockmann); triethylamine : ethyl acetate : petroleum ether 40-60 = 1:9:10) until the impurities were removed according to TLC (aluminium oxide, same eluent, *R<sub>f</sub>* ≈ 0.9). The compound was eluted using ethylacetate : triethyl amine = 9:1. *N*-methyl-*N,N,N*'-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine (L2, 1.743 g, 4.30 mmol, 63 %) was obtained.

<sup>1</sup>H NMR: δ 8.36 (d, *J* = 3.0, 3H), 7.40 - 7.37 (m, 3H), 7.11-7.06 (m, 3H), 3.76 (s, 4H), 3.48 (s, 2H), 2.76 - 2.71 (m, 2H), 2.53 - 2.48 (m, 2H), 2.30 (s, 3H), 2.12 (s, 6H), 2.05 (s, 3H);  
<sup>13</sup>C NMR: δ 156.82, 156.77, 145.83, 145.67, 137.61, 133.14, 132.72, 122.10, 121.88, 62.32, 59.73, 55.19, 51.87, 42.37, 18.22, 17.80.

**[0079] Synthesis of *N*-ethyl-*N,N,N*'-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine (L3, Et-TRILEN).** This synthesis is performed analogously to the synthesis for L2. Starting from 2-hydroxymethyl-3-methyl pyridine (25.00 g, 203 mmol) and *N*-ethyl ethylene-1,2-diamine (2.99 g, 34.0 mmol), *N*-ethyl-*N,N,N*'-tris(methylpyridin-2-ylmethyl)ethylene-1,2-diamine (L3, 11.49 g, 28.5 mmol, 84 %) was obtained. Column chromatography (aluminium oxide; Et<sub>3</sub>N : EtOAc : petroleum ether 40-60 = 1:9:30, followed by Et<sub>3</sub>N : EtOAc = 1:9).

<sup>1</sup>H NMR: δ 8.34 - 8.30 (m, 3H), 7.40 - 7.34 (m, 3H), 7.09 - 7.03 (m, 3H), 3.71 (s, 4H), 3.58 (s, 2H), 2.64 - 2.59 (m, 2H), 2.52 - 2.47 (m, 2H), 2.43 - 2.36 (m, 2H), 2.31 (s, 3H), 2.10 (s, 6H), 0.87 (t, *J* = 7.2, 3H);  
<sup>13</sup>C NMR: δ 157.35, 156.92, 145.65, 137.61, 133.14, 132.97, 122.09, 121.85, 59.81, 59.28, 51.98, 50.75, 48.02, 18.27, 17.80, 11.36.

**[0080] Synthesis of *N*-benzyl-*N,N,N*'-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine (L4, Bn-TRILEN).** This synthesis is performed analogously to the synthesis for L2. Starting from 2-hydroxymethyl-3-methylpyridine (3.00 g 24.4 mmol), and *N*-benzyl ethylene-1,2-diamine (610 mg, 4.07 mmol), *N*-benzyl-*N,N,N*'-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine (L4, 1.363 g, 2.93 mmol, 72 %) was obtained Column chromatography (aluminium oxide; Et<sub>3</sub>N : EtOAc : petroleum ether 40-60 = 1:9:10).

$^1\text{H}$  NMR:  $\delta$  8.33 - 8.29 (m, 3H), 7.37 - 7.33 (m, 3H), 7.21 - 7.03 (m, 8H), 3.66 (s, 4H), 3.60 (s, 2H), 3.42 (s, 2H), 2.72 - 2.67 (m, 2H), 2.50 - 2.45 (m, 2H), 2.23 (s, 3H), 2.03 (s, 6H);

$^{13}\text{C}$  NMR:  $\delta$  157.17, 156.96, 145.83, 145.78, 139.29, 137.91, 137.80, 133.45, 133.30, 128.98, 127.85, 126.62, 122.28, 122.22, 59.99, 58.83, 51.92, 51.54, 18.40, 17.95.

[0081] **Synthesis of *N*-hydroxyethyl-*N,N,N'*-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine (L5).** This synthesis is performed analogously to the synthesis for L6. Starting from 2-hydroxymethyl-3-methyl pyridine (3.49 g, 28.4 mmol), and *N*-hydroxyethyl ethylene-1,2-diamine (656 mg 6.30 mmol), after 7 days *N*-hydroxyethyl-*N,N,N'*-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine (L5, 379 mg, 0.97 mmol, 14 %) was obtained.

$^1\text{H}$  NMR:  $\delta$  8.31 - 8.28 (m, 3H), 7.35 - 7.33 (m, 3H), 7.06 - 7.00 (m, 3H), 4.71 (br s, 1H), 3.73 (s, 4H), 3.61 (s, 2H), 3.44 (t,  $J = 5.1$ , 2H), 2.68 (s, 4H), 2.57 (t,  $J = 5.0$ , 2H), 2.19 (s, 3H), 2.10 (s, 6H);

$^{13}\text{C}$  NMR:  $\delta$  157.01, 156.88, 145.91, 145.80, 137.90, 137.83, 133.30, 131.89, 122.30, 121.97, 59.60, 59.39, 57.95, 56.67, 51.95, 51.22, 18.14, 17.95.

[0082] **Synthesis of *N*-methyl-*N,N,N'*-tris(5-methylpyridin-2-ylmethyl)ethylene-1,2-diamine (L6).** 2-hydroxymethyl-5-methyl pyridine (2.70 g, 21.9 mmol) was dissolved in dichloromethane (25 mL). Thionyl chloride (25 mL) was added dropwise under cooling (ice bath). The resulting mixture was stirred for 1 hour and the solvents removed *in vacuo* (rotavap, until  $p = 20$  mm Hg,  $T \pm 35^\circ\text{C}$ ). The remaining oil was used directly in the synthesis of the ligands, since it was known from the literature that the free picolyl chlorides are somewhat unstable and are highly lachrymatory. To the resultant mixture was added dichloromethane (25 mL) and *N*-methyl ethylene-1,2-diamine (360 mg, 4.86 mmol). Subsequently NaOH (5 N, aq.) was added dropwise. The reaction was quite vigorous in the beginning, since part of the thionyl chloride was still present. The aqueous layer was brought to pH = 10, and additional NaOH (5 N, 4.38 mL) was added. The reaction mixture was stirred until a sample indicated complete conversion (7 days). The reaction mixture was extracted with dichloromethane (3 x 25 mL). The combined organic phases were dried and the solvent removed *in vacuo*. Purification was enforced by column chromatography (aluminium oxide 90 (activity II-III according to Brockmann); triethylamine : ethyl acetate : petroleum ether 40-60 = 1:9:10) until the impurities were removed according to TLC (aluminium oxide, same eluent,  $R_f \approx 0.9$ ). The compound was eluted using ethyl acetate : triethyl amine = 9:1, yielding *N*-methyl-*N,N,N'*-tris(5-methylpyridin-2-ylmethyl)ethylene-1,2-diamine (L6, 685 mg, 1.76 mmol, 36%) as a slightly yellow oil.

$^1\text{H}$  NMR:  $\delta$  8.31 (s, 3H) 7.43 - 7.35 (m, 5H), 7.21 (d,  $J = 7.8$ , 1H), 3.76 (s, 4H), 3.56 (s, 2H), 2.74 - 2.69 (m, 2H), 2.63 - 2.58 (m, 2H), 2.27 (s, 6H), 2.16 (s, 3H);

$^{13}\text{C}$  NMR:  $\delta$  156.83, 156.43, 149.23, 149.18, 136.85, 136.81, 131.02, 122.41, 122.30, 63.83, 60.38, 55.53, 52.00, 42.76, 18.03.

[0083] **Synthesis of *N*-methyl-*N,N,N'*-tris(5-ethylpyridin-2-ylmethyl)ethylene-1,2-diamine (L7).** This synthesis is performed analogously to the synthesis for L6. Starting from 2-hydroxymethyl-5-ethyl pyridine (3.00 g, 21.9 mmol), and *N*-methyl ethylene-1,2-diamine (360 mg, 4.86 mmol), after 7 days *N*-methyl-*N,N,N'*-tris(5-ethylpyridin-2-ylmethyl)ethylene-1,2-diamine (L7, 545 mg, 1.26 mmol, 26 %) was obtained.

$^1\text{H}$  NMR:  $\delta$  8.34 (s, 3H), 7.44 - 7.39 (m, 5H), 7.26 (d,  $J = 6.6$ , 1H), 3.80 (s, 4H), 3.59 (s, 2H), 2.77 - 2.72 (m, 2H), 2.66 - 2.57 (m, 8H), 2.18 (s, 3H), 1.23 (t,  $J = 7.5$ , 9H);

$^{13}\text{C}$  NMR:  $\delta$  157.14, 156.70, 148.60, 148.53, 137.25, 135.70, 122.59, 122.43, 63.91, 60.48, 55.65, 52.11, 42.82, 25.73, 15.36.

#### Synthesis of metal-ligand complexes:

[0084] **Synthesis of *N*-methyl-*N,N,N'*-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine iron(II)chloride. $\text{PF}_6$  ([L2 Fe(II)Cl]PF<sub>6</sub>).** FeCl<sub>2</sub>·4H<sub>2</sub>O (51.2 mg, 257  $\mu\text{mol}$ ) was dissolved in MeOH : H<sub>2</sub>O = 1:1 (2.5 mL). The solution was heated to 50 °C. Added was *N*-methyl-*N,N,N'*-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine (L2, 100 mg, 257  $\mu\text{mol}$ ) in MeOH : H<sub>2</sub>O = 1:1 (2.0 mL). Subsequently NaPF<sub>6</sub> (86.4 mg, 514  $\mu\text{mol}$ ) in H<sub>2</sub>O (2.5 mL) was added dropwise. Cooling to room temperature, filtration and drying *in vacuo* ( $p = 0.05$  mm Hg,  $T =$  room temperature) yielded the complex [L2 Fe(II)Cl]PF<sub>6</sub> (149 mg, 239  $\mu\text{mol}$ , 93 %) as a yellow solid.

$^1\text{H}$ NMR (CD<sub>3</sub>CN, paramagnetic):  $\delta$  167.17, 142.18, 117.01, 113.34, 104.79, 98.62, 70.77, 67.04, 66.63, 58.86, 57.56, 54.49, 51.68, 48.56, 45.90, 27.99, 27.36, 22.89, 20.57, 14.79, 12.14, 8.41, 8.16, 7.18, 6.32, 5.78, 5.07, 4.29, 3.82, 3.43, 2.91, 2.05, 1.75, 1.58, 0.94, 0.53, -0.28, -1.25, -4.82, -18.97, -23.46.

**[0085]** Synthesis of *N*-ethyl-*N,N',N'*-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine iron(II)chloride.PF<sub>6</sub> ([L3 Fe(II)Cl]PF<sub>6</sub>). This synthesis was performed analogously to the synthesis for [L2 Fe(II)Cl]PF<sub>6</sub>. Starting from *N*-ethyl-*N,N',N'*-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine (L3, 104 mg, 257 μmol) gave the complex [L3 Fe(II)Cl]PF<sub>6</sub> (146 mg, 229 μmol, 89%) as a yellow solid.

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<sup>1</sup>H NMR (CD<sub>3</sub>CN, paramagnetic): δ 165.61, 147.20, 119.23, 112.67, 92.92, 63.14, 57.44, 53.20, 50.43, 47.80, 28.59, 27.09, 22.48, 8.55, 7.40, 3.63, 2.95, 2.75, 2.56, 2.26, 1.75, 1.58, 0.92, 0.74, -0.28, -1.68, -2.68, -12.36, -28.75.

10 **[0086]** Synthesis of *N*-benzyl-*N,N',N'*-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine iron(II)chloride.PF<sub>6</sub> ([L4 Fe(II)Cl]PF<sub>6</sub>). This synthesis was performed analogously to the synthesis for [L2 Fe(II)Cl]PF<sub>6</sub>. Starting from *N*-benzyl-*N,N',N'*-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine (L4, 119.5 mg, 257 μmol) gave the complex (172 mg, 229 μmol, 95 %) as a yellow solid.

15 <sup>1</sup>H NMR (CD<sub>3</sub>CN, paramagnetic): δ 166.33, 145.09, 119.80, 109.45, 92.94, 57.59, 52.83, 47.31, 28.40, 27.89, 16.28, 11.05, 8.70, 8.45, 7.69, 6.99, 6.01, 4.12, 2.89, 2.71, 1.93, 1.56, -0.28, -1.68, -2.58, -11.40, -25.32.

### Experimental:

20 **[0087]** Experiments were carried out in a temperature-controlled glass beaker equipped with a magnetic stirrer, thermocouple and a pH electrode. The bleach experiments are carried out at 40 and 60 °C. In examples when formulations are used, the dosage amounted to about 5 g/l total formulation. The composition of the base formulation without bleach is described below:

### 25 Detergent formulation

#### **[0088]**

	Anionic surfactant:	9%
30	Nonionic surfactant:	7%
	Soap:	1%
	Zeolite:	30%
	Polymers:	3%
	Sodium carbonate:	7%
35	Enzyme granules:	1%
	Sodium silicate:	5%
	Sodium citrate:	3.5%
	Dequest® 2047:	1%
	Percarbonate:	19%
40	TAED granule (83%)	5.5%
	Water and minors:	8%

**[0089]** In total 8.6 mmol/l H<sub>2</sub>O<sub>2</sub> was used, dosed in the form of sodium percarbonate. The pH was adjusted at 10.0. The bleaching process took place for 30 minutes.

45 **[0090]** Tea-stained test cloths (BC-1) were used as bleach monitor. After the bleach experiment, the cloths were rinsed in tap water and dried in a tumble drier. The reflectance (R<sub>460</sub>\*) was measured before and after the wash on a Minolta® CM 3700d spectrophotometer. The average was taken of 2 test cloths. The differences in reflectance, expressed as ΔR values, are given in the tables below.

### 50 Example 1

**[0091]** Ligand/metal salt mixtures were dosed at a concentration of 10 μmol/l iron perchlorate and 50 μmol/l of ligand. These mixtures were prepared by dissolving the iron salt and ligand in ethanol. 10 ml of this stock solution was added to the bleach solution.

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	$\Delta R$ :
H <sub>2</sub> O <sub>2</sub> (no buffer):	7.4 points
Fe-perchlorate + L1:	13.7 points
Fe-perchlorate + L2:	16.8 points
Fe-perchlorate + L3:	16.3 points
Fe-perchlorate + L4:	14.3 points
Fe-perchlorate + L5:	14.0 points
Fe-perchlorate + L6:	13.2 points
Fe-perchlorate + L7:	13.5 points

[0092] These results show a clear benefit of these complexes with respect to the blank. The mixtures using ring-substituted ligands L2 to L5, in particular L2 ("Me-Trilen") and L3 ("Et-Trilen"), show benefit compared with the ring-unsubstituted ligand L1 ("Trispicen").

#### Example 2

[0093] Well-defined metal-ligand complexes were dosed using the same set up as Example 1, except using 10  $\mu$ M catalyst, at 40 °C, with 8.8 mmol/l H<sub>2</sub>O<sub>2</sub>, no buffer, pH 10.0:

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	$\Delta R$ :
- no catalyst:	6.5 points
- [Fe(L2)Cl]PF <sub>6</sub> :	15.7 points
- [Fe(L3)Cl]PF <sub>6</sub> :	14.8 points
- [Fe(L4)Cl]PF <sub>6</sub> :	12.7 points

#### Example 3

[0094] Well-defined metal-ligand complexes were dosed using the same set up as Example 2, at 40 °C, except using 5  $\mu$ M catalyst, with 8.8 mmol/l H<sub>2</sub>O<sub>2</sub> in 10 mmol/l carbonate buffer, pH 10.0:

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	$\Delta R$ :
- no catalyst:	7.4 points
- [Fe(L2)Cl]PF <sub>6</sub> :	15.9 points
- [Fe(L3)Cl]PF <sub>6</sub> :	14.4 points
- [Fe(L4)Cl]PF <sub>6</sub> :	11.3 points

#### Example 4

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[0095] Well-defined metal-ligand complexes were dosed using the same set up as Example 3, at 40 °C, except in the presence of 5 g/L detergent formulation without TAED (8.8 mmol/l H<sub>2</sub>O<sub>2</sub>, pH 10.0):

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	$\Delta R$ :
- no catalyst:	8.6 points
- [Fe(L2)Cl]PF <sub>6</sub> :	14.9 points
- [Fe(L3)Cl]PF <sub>6</sub> :	14.4 points
- [Fe(L4)Cl]PF <sub>6</sub> :	11.1 points

Example 5

- 15 [0096] Well-defined metal-ligand complexes were dosed using the same set up as Example 3, except in the presence of 5 g/L detergent formulation with TAED (yielding 8.7 mmol/l H<sub>2</sub>O<sub>2</sub> and 2 mmol/l peracetic acid):

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	$\Delta R$ :
- no catalyst:	11.3 points
- [Fe(L2)Cl]PF <sub>6</sub> :	19.6 points
- [Fe(L3)Cl]PF <sub>6</sub> :	17.4 points

Example 6

- 30 [0097] Well-defined metal-ligand complexes were dosed using the same set up as Example 3, but at 60 °C:

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	$\Delta R$ :
- no catalyst:	12.7 points
- [Fe(L2)Cl]PF <sub>6</sub> :	21.6 points
- [Fe(L3)Cl]PF <sub>6</sub> :	19.1 points
- [Fe(L4)Cl]PF <sub>6</sub> :	15.3 points

Example 7

- 45 [0098] Well-defined metal-ligand complexes were dosed using the same set up as Example 6, at 60 °C, except in the presence of 5 g/L detergent formulation without TAED:

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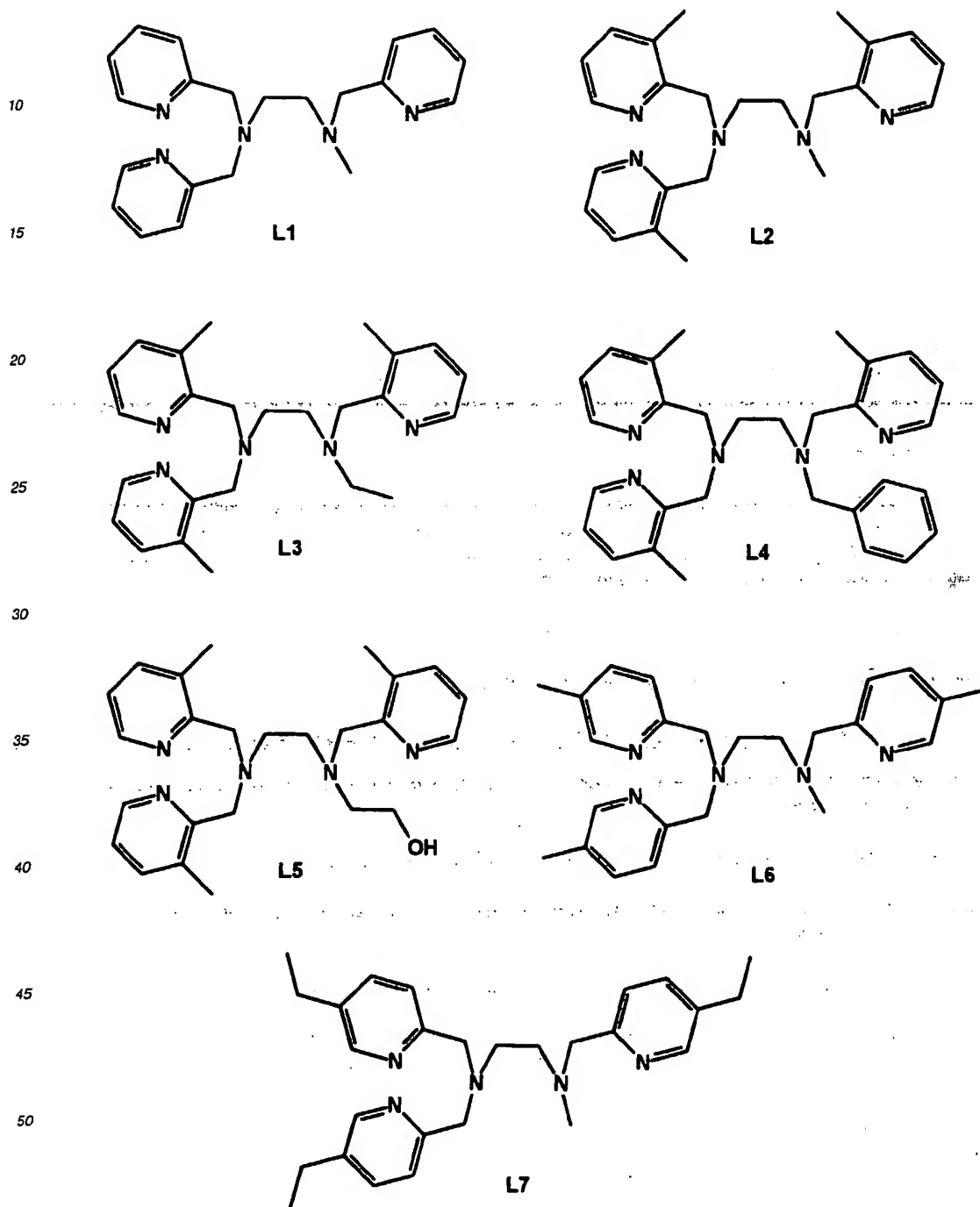
	$\Delta R$ :
- no catalyst:	14.2 points
- [Fe(L2)Cl]PF <sub>6</sub> :	20.5 points
- [Fe(L3)Cl]PF <sub>6</sub> :	18.8 points
- [Fe(L4)Cl]PF <sub>6</sub> :	16.5 points

- [0099] These results show that the well-defined Fe-ligand complexes provide high bleaching activity, similar to

those of Fe-salt/ligand mixtures. The activity ranks as Me-Trilen > Et-Trilen > Bz-Trilen. The complex catalysts are also active in detergent formulations, with or without TAED. Also, the complex catalysts are active at 60 °C, both in the absence or presence of a formulation.

[0100] The structures of the ligands L1 to L7 is shown below:

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## Claims

1. A bleach and oxidation catalyst comprising a complex of the general formula (A):



in which

- M represents iron in the II, III, IV or V oxidation state, manganese in the II, III, IV, VI or VII oxidation state, or copper in the I, II or III oxidation state;  
 X represents a coordinating species;  
 n represents zero or an integer in the range from 0 to 3;  
 z represents the charge of the complex and is an integer which can be positive, zero or negative;  
 Y represents a counter ion, the type of which is dependent on the charge of the complex;  
 $q = z/[charge\ Y]$ ;  
 L represents a pentadentate ligand of general formula (B):



- wherein  
 each  $R^1$  independently represents  $-R^3-V$ , in which  $R^3$  represents optionally substituted alkylene, alkenylene, oxyalkylene, aminoalkylene or alkylene ether, and V represents a substituted heteroaryl group selected from pyridinyl, pyrazinyl, pyrazolyl, imidazolyl, benzimidazolyl, pyrimidinyl, triazolyl and thiazolyl;  
 W represents an optionally substituted alkylene bridging group selected from  $-CH_2CH_2-$ ,  $-CH_2CH_2CH_2-$ ,  $-CH_2CH_2CH_2CH_2-$ , and  $-CH_2-C_6H_4-CH_2-$ ;  
 $R^2$  represents a group selected from alkyl and aryl, optionally substituted with a substituent selected from hydroxy, alkoxy, carboxylate, carboxamide, carboxylic ester, sulphonate, amine, alkylamine and  $N^+(R^4)_3$ , wherein  $R^4$  is selected from hydrogen, alkanyl, alkenyl, arylalkanyl, arylalkenyl, oxyalkanyl, oxyalkenyl, aminoalkanyl, aminoalkenyl, alkanyl ether and alkenyl ether.

2. A catalyst according to claim 1, wherein M is iron in the II, III, IV or V oxidation state.
3. A catalyst according to claim 1 or claim 2, wherein W represents ethylene.
4. A catalyst according to any preceding claim, wherein V represents substituted pyridin-2-yl.
5. A catalyst according to any preceding claim, wherein  $R^3$  represents methylene and V represents methyl-substituted or ethyl-substituted pyridin-2-yl.
6. A catalyst according to any preceding claim, wherein V represents 3-methyl pyridin-2-yl.
7. A catalyst according to any preceding claim, wherein  $R^2$  represents a group selected from methyl, ethyl, benzyl, 2-hydroxyethyl, and 2-methoxyethyl.
8. A catalyst according to claim 7, wherein  $R^2$  represents a group selected from methyl and ethyl.
9. A catalyst according to any preceding claim, wherein the ligand L is N-methyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine or N-ethyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine.
10. A catalyst according to any preceding claim, wherein X represents a coordinating species selected from  $CH_3CN$ ,  $H_2O$ ,  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $OOH^-$ ,  $O_2^{2-}$ ,  $O_2^-$ ,  $R^5COO^-$ ,  $R^5O^-$ ,  $LMO^-$ , and  $LMOO^-$  wherein  $R^5$  represents hydrogen or optionally substituted phenyl, naphthyl, or  $C_1-C_4$  alkyl.
11. A catalyst according to any preceding claim, wherein the counter ion Y is selected from  $R^6COO^-$ ,  $ClO_4^-$ ,  $BF_4^-$ ,  $PF_6^-$ ,  $R^6SO_3^-$ ,  $R^6SO_4^-$ ,  $SO_4^{2-}$ ,  $NO_3^-$ ,  $F^-$ ,  $Cl^-$ ,  $Br^-$ , and  $I^-$ , wherein  $R^6$  represents hydrogen or optionally substituted phenyl, naphthyl or  $C_1-C_4$  alkyl.
12. A composition comprising a ligand L or a ligand L-generating species, and a salt of the metal M, wherein a catalyst



as defined in any preceding claim is formed *in situ*.

13. A composition comprising a peroxy bleaching compound and a catalyst as defined in any of the preceding claims.
- 5 14. A composition according to claim 13, which comprises the peroxy bleaching compound at a level of from 2 to 35% by weight and the catalyst at a level corresponding to a metal content of from 0.0005 to 0.5% by weight.
- 15 15. A composition according to claim 13 or claim 14, wherein the peroxy bleaching compound is selected from hydrogen peroxide, hydrogen peroxide-liberating or -generating compounds, peroxyacids and their salts, and mixtures thereof, optionally together with peroxyacid bleach precursors.
16. A composition according to any of claims 13 to 15, further comprising a surface-active material and a detergency builder.
- 15 17. A composition according to claim 16, comprising the surface-active material in an amount of from 10 to 50% by weight, and the detergency builder in an amount of from 5 to 80% by weight.

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## EUROPEAN SEARCH REPORT

Application Number  
EP 98 30 9169

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,X	WO 97 48787 A (UNILEVER PLC ;UNILEVER NV (NL)) 24 December 1997  * page 5, line 25 - line 36 * * claims 1-11 *	1-4,7, 10,11, 13-17	C11D3/395 D06L3/02 C07F15/02 C07F1/08 C07F13/00 B01J31/18
D,X	WO 97 18035 A (ELF AQUITAINE ;FRAISSE LAURENT (FR); GIRERD JEAN JACQUES (FR); PER) 22 May 1997  * page 7, line 15 - line 20 * * claims 1-28 *	1-5,7,8, 10,11, 13,15	
D,A	WO 95 34628 A (UNILEVER NV ;UNILEVER PLC (GB)) 21 December 1995  * claims 1-9 *	1-17	
A	EP 0 458 398 A (UNILEVER NV ;UNILEVER PLC (GB)) 27 November 1991  * page 20; example IV * * claims 1-28 *	1-17	
A	DE 196 05 688 A (HENKEL KGAA) 21 August 1997  * page 2, line 46 - page 5, line 64 *	1-17	TECHNICAL FIELDS SEARCHED (Int.Cl.6)  C11D D06L B01J
A	DE 197 13 851 A (HENKEL KGAA) 8 October 1998  * page 2, line 52 - page 4, line 62 *	1-17	
A	FR 2 692 499 A (ATOCHEM ELF SA) 24 December 1993  * claims 1-15 *	1-17	
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>9 April 1999</b>	Examiner <b>Richards, M</b>
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 98 30 9169

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
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09-04-1999

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9748787	A	24-12-1997	AU 2892897 A	07-01-1998
			CA 2257891 A	24-12-1997
			EP 0906402 A	07-04-1999
WO 9718035	A	22-05-1997	FR 2741340 A	23-05-1997
			AU 7628996 A	05-06-1997
			CA 2235764 A	22-05-1997
			NO 982240 A	16-07-1998
WO 9534628	A	21-12-1995	AU 2614895 A	05-01-1996
			BR 9507984 A	18-11-1997
			EP 0765381 A	02-04-1997
			US 5580485 A	03-12-1996
EP 0458398	A	27-11-1991	AU 622362 B	02-04-1992
			AU 7712691 A	21-11-1991
			AU 622363 B	02-04-1992
			AU 7712791 A	21-11-1991
			CA 2042736 A,C	22-11-1991
			CA 2042738 A,C	22-11-1991
			DE 69125309 D	30-04-1997
			DE 69125309 T	03-07-1997
			DE 69125310 D	30-04-1997
			DE 69125310 T	03-07-1997
			EP 0458397 A	27-11-1991
			ES 2100924 T	01-07-1997
			ES 2100925 T	01-07-1997
			IN 172881 A	25-12-1993
			JP 2613707 B	28-05-1997
			JP 6269676 A	27-09-1994
			JP 2042652 C	09-04-1996
			JP 4270798 A	28-09-1992
			JP 7065074 B	12-07-1995
			KR 9501045 B	08-02-1995
DE 19605688	A	21-08-1997	WO 9730144 A	21-08-1997
			EP 0880579 A	02-12-1998
DE 19713851	A	08-10-1998	NONE	
FR 2692499	A	24-12-1993	AT 157024 T	15-09-1997
			AU 671284 B	22-08-1996
			AU 4333393 A	24-01-1994

EPO FORM P0459 For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 98 30 9169

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The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

09-04-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR 2692499    A		BR    9306591 A	08-12-1998
		CA    2138797 A	06-01-1994
		DE    69313284 D	25-09-1997
		EP    0647158 A	12-04-1995
		FI    945990 A	21-02-1995
		WO    9400234 A	06-01-1994
		JP    8500856 T	30-01-1996
		NZ    253184 A	26-09-1995
		US    5630906 A	20-05-1997
-----			

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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